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Original scientific paper

Comparative investigation of the sweet and bitter orange essential oil (*Citrus sinensis* and *Citrus aurantium*)

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Abstract

The volatile fraction composition of commercially produced sweet and bitter orange oil from fruit peels was studied using GC-MS. More than fifty components were identified in the oils using their mass spectra and linear retention indices. The monoterpene limonene was the most abundant component even though not in a quantity expected for a fresh orange essential oil. Aldehydes, followed by alcohols and esters, were the main components in the oxygenated fraction. Aldehydes were the major oxygenated components in the sweet orange oil, whereas alcohols and esters were present in higher amounts in the bitter orange oil. Among them, nonanal, decanal and linalool are the most important components for the flavour of sweet orange oil and carvon is the most important ketone for the flavour of bitter orange oil in combination with the other components. The amount of carvon gives a good indication about the freshness of the oil and the quantities of α-pinene and β-pinene, sabinene and myrcene give an indication about the natural or artificially changed composition of the essential oils.

Key words: *Citrus sinensis*, *Citrus aurantium*, peel oil, GC-MS, volatile components

Introduction

Cold pressed orange oil is widely used in beverage, perfumery industry and aromatherapy. In general, there are two types of orange oils: sweet orange oil from *Citrus sinensis* and bitter orange oil from *Citrus aurantium*.

Sweet orange oil is the most widely used citrus oil. It possesses a light sweet, fresh top note with fruity and aldehydic character (1). It is widely used in the flavour industry especially in beverages and candies. It can provide the top note for citrus flavouring as well as characteristic and most universally accepted flavour. The sweetness and in the same time the refreshing note makes them appropriate base for still and carbonated soft drinks.

Most of the orange oils on the world market are Italian and American industrial oils, but there are also oils produced in Spain, and in the South American countries. Moreover, studies on laboratory-extracted oils from the peel of fruits of special cultivars from different regions such as Algeria, Libya, Israel, Russia, China and Japan have been published (1).

Bitter orange oil possesses fresh citrus top notes, but is considered less sweet, and even bitter and dry. It has floral and aldehydic characteristics (1). The tenacity is greater than the most other citrus oils. In flavourings, this oil can be used to provide a citrus top note or act as a modifier in the citrus blend. The major application is in the citrus flavourings for beverages, especially liqueurs. It also intensifies the orange character in soft drinks.

Most of the papers pertinent to sweet orange oil composition were reviewed by Sawamura (2, 3) and Lawrence (4). A large number of papers deal with the composition of the volatile fraction of sweet orange oil and in many of them its differences in relation to the cultivars are reported with particular references to the different content of aliphatic aldehydes and linalool (5-10), and the volatile components of bitter orange oil (11,12).

The goal of this work is to present a way of comparative investigation of the cold pressed sweet and bitter

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orange oils found in the market and to see the difference between the oils. The results are compared with the published ones for fresh orange oils and some indications about the freshness and the origin are discussed.

Experimental

Two commercial samples of oils produced from peel of *Citrus sinensis* and *Citrus aurantium* were kindly supplied from an Italian flavour company.

Each sample was analysed by GC/MS using a HP 6890 Gas chromatograph equipped with a HP 5973 mass selective detector with a HP-5 fused silica column (30 m x 0.25mm, 0.25 μm film thickness). The column temperature was changed linearly from 40 to 180 °C by 4 °C/min, and after that 20°C/min to 260°C. 0.2 μL were injected at a split ratio of 1:100. The inlet temperature was 260°C and the transfer line temperature was 280°C.

The MS library used was Wiley 275. Also, compound identification was checked by linear retention indices with standard series of alkanes (C_8-C_{32}) and compared with the LRI values in the database of the Citrus Research and Education Centre at the University of Florida (13) and in the book of Adams (14).

Results and discussion

Sample preparation is one of the most important processes in flavour research, because the aroma compounds are substantially volatile and unstable against heat (3). GC-MS is a valuable tool in characterization of essential oils because the interpretation of the results of qualitative and quantitative analysis can enable an insight in the process of production, storage and age of the commercially produced oils.

In this work, more than fifty components were identified in the analysed sweet and bitter orange oils. The identified compounds and their linear retention indices calculated on HP-5 column are given in Table 1. For each sample, the quantitative composition (as a relative percentage of peak area) for each component is given together with the aroma descriptors for the components as found in the database of the Citrus Research and Education Centre at the University of Florida (13) and by Choi (15).

The GC-MS chromatograms obtained for both samples of essential oils of sweet and bitter orange oil are given in Fig. 1 and Fig. 2, respectively.

The data in Table 1 show that different quantities and ratios of the same components give different taste of the aroma. According to the data, the quantities of α-pinene,

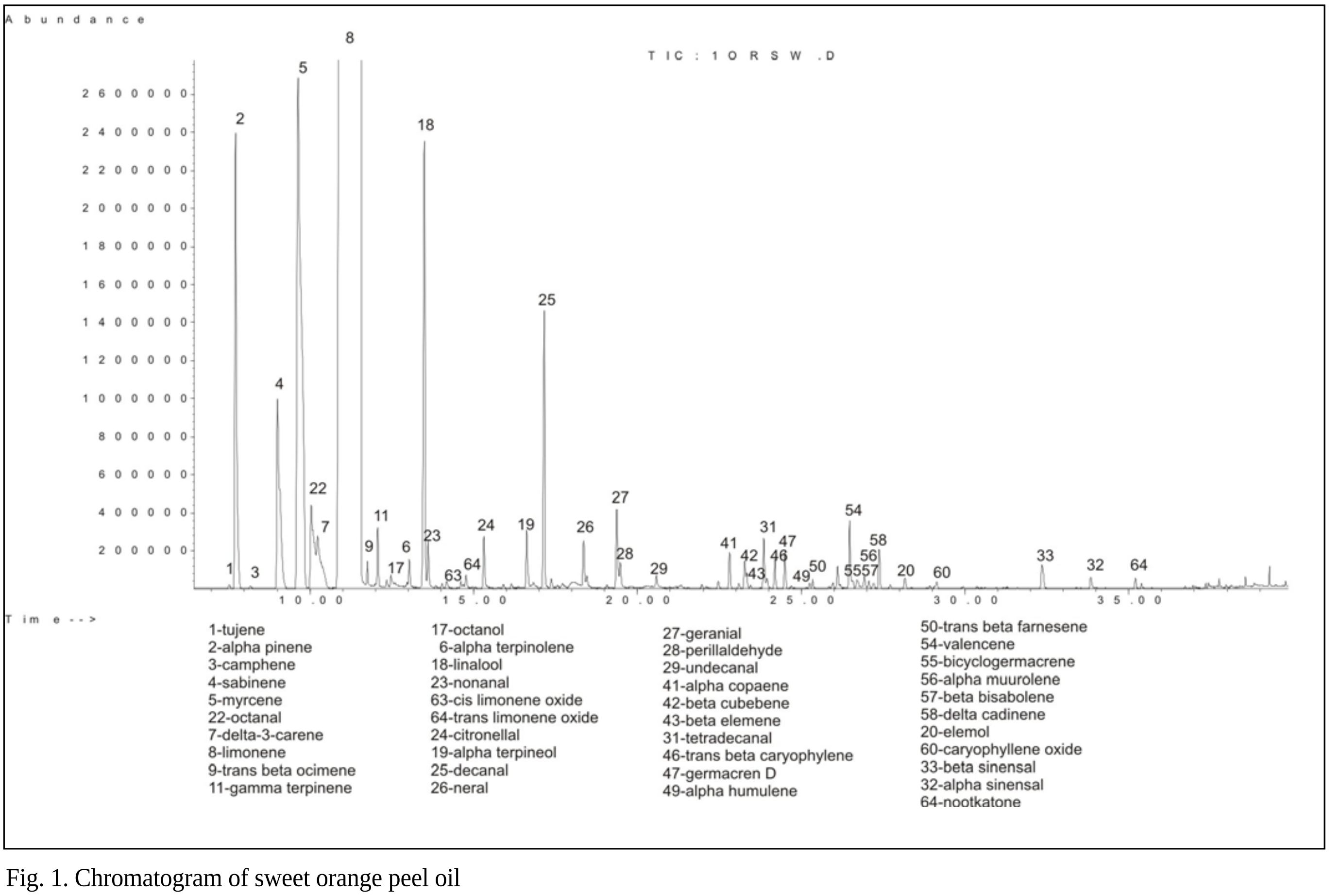

Fig. 1. Chromatogram of sweet orange peel oil

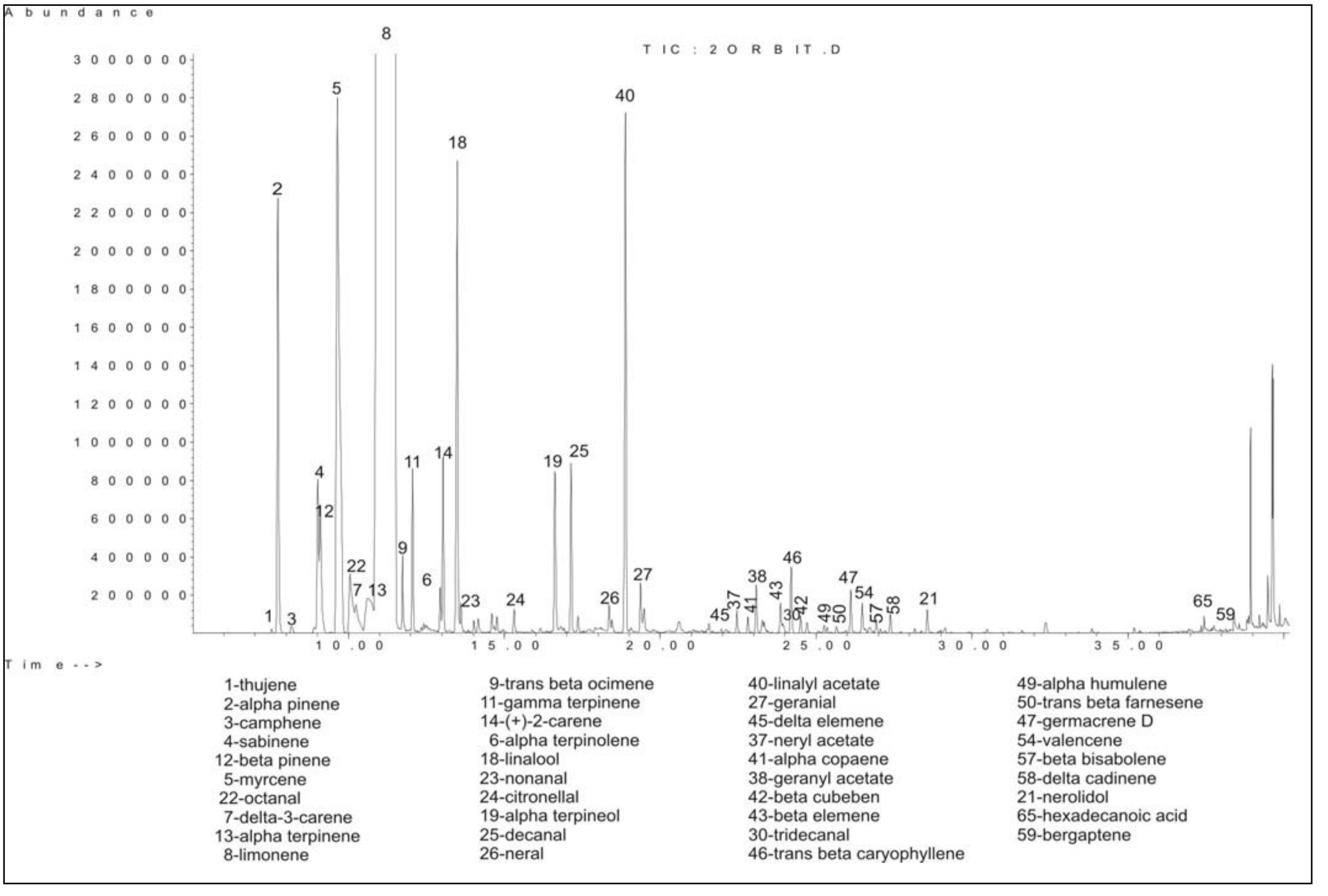

Fig. 2. Chromatogram of bitter orange peel oil

camphene, myrcene and octanal are higher than the usual values for cold-pressed sweet and bitter orange oil (1). On the other hand, the quantities of limonene are lower (76.65 % in sweet orange oil and 71.2 % in bitter orange oil) than expected according to the published data for fresh sweet and bitter orange essential oils (over 90 %) (1).

The quantity of α-terpinolene which gives the citrus and pine note according to odor description database of Citrus Research and Education Centre (13) is almost six times greater in bitter orange oil than in sweet orange oil. The quantity of valencene in sweet orange oil is more than double compared to bitter orange oil, which is expected because this compound gives the specific sweet citrus odor for sweet orange.

Aldehydes are the most important compounds for the citrus flavour. The quantity of aldehydes in sweet orange peel oil is double compared to the aldehydes content in the bitter orange oil. Octanal, nonanal and decanal, which are very active odor compounds and have a sweet note, are in higher quantity in sweet than in bitter orange oil (2).

On the other hand, alcohols content in bitter orange oil is higher than in sweet orange oil, but linaool in both analysed commercial oils is in bigger quantity than expected from the published data (1).

Also the quantity of esters is three times higher in bitter orange oil in comparison to quantity of esters in sweet orange oil, because the quantity of geranyl acetate and linalyl acetate are very high in bitter orange oil.

There are some components expected and identified in the in bitter orange oil like +-2-carene, n-octyl acetate, linalyl acetate, 2,4-decadienal, δ-elemene, germacren B, nerolidol, bergapten, which are missed in the sweet orange oil. β-pinene is also missed in sweet orange oil and it is present in bitter orange oil in enough high quantity.

It is well known that the bitter taste of bitter orange oil predominantly comes from the nonvolatile components of the peel, but also the volatile components give a significant part of the aroma of bitter orange oil (1). The component which gives a bitter odor, carvon, is in higher quantity in bitter orange than in sweet orange oil. It has been observed that orange oil deteriorates very rapidly in aqueous acidic environment and under the influence of light and oxygen. Relatively high quantity of carvon in both oils has been identified as the major degradation product (Fig. 3), and has also been reported as a constituent of various old citrus oils (11, 16). From this we can include that the oils purchased from the market are not fresh.

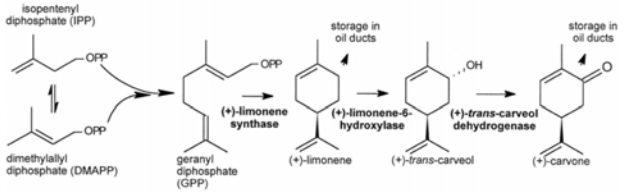

Fig. 3. Biosynhesis of limonene and its transformation to carvone during storage

All these results indicate that the two commercially produced orange oils purchased from the flavour market are not fresh and original cold pressed essential oils, but some of the components, like limonene, are removed from the oil and some of the components, like α-pinene, sabinene are added to the oils by physical or chemical methods (1).

In conclusion, the qualitative and quantitative analysis of the commercial bitter orange oil shows that this oil is not pure cold pressed oil because the ratio α-pinene/β-pinene is greater then 0.8 which indicates addition of grapefruit terpenes in the bitter orange oil (1). On the other hand, the significant amount of myrcene (>2 %) and octanal (>0.2 %) in the commercial sweet orange oil gives an indication that the oil is not an original cold pressed oil, but has been modified in the manufacturing process, which is also supported by the significantly reduced content of limonene.

Table 1. Percentage composition as single components for the two different orange oils, the LRI index for each component of HP-5 column and aroma descriptors

	Component	LRI	% in C. sinensis	% in C. aurantium	Aroma descriptor [13, 15]
	Monoterpenes				
1.	á-tuje ne	926	0.02	0.02	
2.	á-pinene	932	2.57	2.10	pine-like, resinous, green, sweet
3.	camphene	947	0.01	0.06	warm, oily, camporaceous
4.	sabinene	972	1.83	0.84	warm, oily, peppery, green
5.	myrcene	992	6.90	5.86	musty, wet soil
6.	á-terpinolene	1090	0.13	0.77	citrus, pine
7.	ä-3-carene	1010	0.79	0.37	sweet
8.	limonene	1033	76.65	71.2	citrus-like, fresh
9.	trans-â-ocimene	1054	0.10	0.32	herbacous, flowery, sweet, warm
10.	â-phellandrene	1060	0.01	-	citrus-like, fresh
11.	ã-terpinene	1062	0.23	0.67	lemony, lime-like
12.	â-pinene	975		0.79	resinous, dry, woody
13.	á-terpinene	1021		0.05	lemony, citrusy
14.	+-2-carene	1088		0.20	
15.	ä-4-carene	1351		0.02	
	Total		89.24	83.27	
	hydrates				
16.	cis-sabinene hydrate	1070	0.03	0.04	
	Total		0.03	0.04	
	alcohols				
17.	octanol	1074	0.07	0.11	soapy
18.	linalool	1103	2.30	2.50	floral, green, citrus
19.	á-terpineol	1192	0.31	0.83	floral, lilac-like
18.	nerol	1233	0.07	-	fruity, floral
20.	elemol	1552	0.06	0.02	sweet, woody, faint
21.	nerolidol	1566		0.12	woody, floral, mild
	Total		2.81	3.58	
	aldehydes				
22.	octanal	1004	0.96	0.67	fatty, tallowy, citrus-like
23.	nonanal	1107	0.22	0.17	piney, floral, citrusy
24.	citronellal	1155	0.25	0.12	powerful, floral, lemon
25.	decanal	1208	1.27	0.78	beefy, musty, marine, cucumber

26.	neral	1243	0.24	0.15	lemony, citrusy
27.	geranial	1273	0.42	0.27	citrus-like, flowery, fruity
28.	perillaldehyde	1276	0.14	-	
29.	undecanal	1309	0.08	-	pleasant waxy, floral
30.	tridecanal	1410	0.24	0.15	waxy, fresh, citrusy, powerful
31.	tetradecanal	1614	0.01	-	fresh, herbaceous
32.	á-sinensal	1757	0.06	0.02	orange-like
33.	â-sinensal	1700	0.17	0.08	orange peel
34.	2,4-decadienal	1319		0.02	geranium, powerful
35.	3-dodecen-1-al	1468		0.04	
	Total		4.06	2.47	
	esters				
36.	citronellyl acetate	1356	0.01	-	fresh, rosy, fruity
37.	neryl acetate	1367	0.02	0.12	fruity, floral, very sweet
38.	geranyl acetate	1386	0.02	0.22	dry, herbaceous
39.	n-octyl acetate	1214		0.09	fruity, slightly fatty
40.	linalyl acetate	1259		2.54	floral-fruity
	Total		0.05	2.97	
	sesquiterpenes				
41.	á-copaene	1377	0.16	0.08	
42.	â-cubebene	1392	0.18	0.07	fruity, green
43	â-elemene	1394	0.07	0.06	fruity
44.	aromadendrene	1397	0.02	-	
45.	ä-elemene	1339		0.05	
46.	trans-â-caryophyllene	1421	0.14	0.32	citrus-like, fresh
47.	germacrene-D	1483	0.11	0.22	
48.	trans-á-bergamotene	1437	0.01	0.06	
49.	á-humulene	1455	0.03	0.04	woody
50.	trans-â-farnesene	1458	0.04	0.03	sweet, fruity
51.	á-amorphene	1478	0.03	0.02	
52.	germacrene-B	1559	0.04	0.01	
53	â-selinene	1485	0.01	0.01	
54.	valencene	1495	0.34	0.15	sweet, woody, citrusy
55.	bicyclogermacrene	1498	0.04	0.03	
56.	á-muurolene	1510	0.07	-	
57.	â-bisabolene	1519	0.07	0.07	
58.	ä-cadinene	1526	0.19	0.09	woody, dry, mild
59.	bergapten	-		0.12	
	Total		1.55	1.43	
	oxides				
60.	caryophillene oxide	1585	0.04	0.03	woody, spicy
61.	cis-limonene oxide	1135	0.03	0.09	citrus like
62.	trans-limonene oxide	1140	0.07	0.09	citrus like
	Total		0.14	0.21	
	ketones				
63.	carvone	1246	0.07	0.09	bitter, spearmint, caraway
64.	nootkatone	1808	0.05	0.03	green, grapefruit
	Total		0.13	0.12	
	acids				
65.	hexadecanoic acid	1890	0.03	0.06	
	Total		0.03	0.06	

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Резиме

Споредбено испитување на етерични масла од сладок и горчлив портокал

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Клучни зборови: *Citrus sinensis, Citrus aurantium,* масло од кора од портокал, GC-MS, испарливи компоненти

Испитуван е составот на испарливата фракција на масло од кората на комерцијални примероци од горчлив и сладок портокл, користејќи ја техниката на гасна хроматографија со масена спектрометрија. Идентификувани се повеќе од 50 компоненти во согласност со нивните масени спектри и релативни ретенциски индекси. Најзастапена компонента е монотерпенот лимонен но не во количините кои можат да бидат очекувани од свежо етерично масло од портокал. Алдехиди, а потоа алкохоли и естери се главните компоненти во оксигенирана фракција на маслото. Во маслото од сладок портокал, алдехидите се доминантни оксигенирани компоненти додека во маслото од горчлив портокал алкохолите и естрите се пронајдени во поголемо количество. Најбитни компоненти за мирисот на етеричното масло од сладок портокал се нонанал, деканал и линалол а за маслото од горчливиот портокал тоа е кетонот карвон во комбинација со други компоненти. Количеството на карвон е индикатор за свежината и староста на маслото додека од количествата и соодносот на α - пинен, β - пинен, сабинен и мирцен може да се процени дали има вештачки промени во природниот состав на етерично масло.